



Scholars Research Library

Archives of Applied Science Research, 2013, 5 (4):12-16  
(<http://scholarsresearchlibrary.com/archive.html>)



## Excess thermodynamic parameters of Acrylonitrile with methanol, 1,4-dioxane and cyclohexane at 303K

\*Bhandakkar V. D., Shweta Rode and #Sangita Jajodia

\*Department of Electronic, Anand Niketan College, Warora

#Department of Physics, Chouksey Engineering College, Bilaspur (CG)

### ABSTRACT

The result of a new experimental study of thermo-acoustic properties for the binary systems of acrylonitrile with methanol, 1,4-dioxane and cyclohexane have been presented. The density ( $\rho$ ), viscosity ( $\eta$ ) and velocity ( $U$ ) have been measured over the whole range of composition at the temperature 303K. These properties have been used to determine the excess parameters such as excess adiabatic compressibility ( $\beta_a^E$ ), excess free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), excess internal pressure ( $\pi_i^E$ ), excess relaxation time ( $\tau^E$ ), excess acoustic impedance ( $Z_a^E$ ) and excess Gibbs' s ( $\Delta G^E$ ). The non-ideal behavior of these binary systems has been revealed through the sign and magnitude of the excess parameters. These parameters have been studied on the basis of dipole-dipole interactions and hydrogen bonding as well as the nature and the strength of interactions in the binary mixtures are discussed.

**Keywords:** Ultrasonic velocity, acoustical parameters, molecular interactions, binary mixtures, Acrylonitrile, methanol, 1,4-dioxane, cyclohexane and excess parameters.

### INTRODUCTION

Ultrasonic velocity in the binary liquids mixtures is very sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interactions [1-3]. The physical and chemical properties of liquids mixtures have been correlated to the nonlinear variation of ultrasonic velocity and other related acoustic and excess thermo-acoustic parameters [4, 5]. Hydrogen bonded systems are very interesting because hydrogen bond play a vital role in chemical, physical and biological processes [6]. The study of molecular associations in organic mixtures having alcohol is one of the component is of particular interest since alcohols are strongly self associated liquids with a hydrogen bonds[7] and can be associated with any other group having some degree of polar attraction [8]. Acrylonitrile is an industrially significant organic compound [9]. The excess thermo-acoustic properties and molecular interactions in the binary liquids mixtures of industrially important acrylonitrile with alcohol methanol and non-polar liquids 1,4-dioxane & cyclohexane has been studied in the present paper. The liquid mixed, results in a non-ideal mixture because of specific interaction between component molecules [10-15].

In the present study ultrasonic velocity, density and viscosity have been measured experimentally for the binary systems namely *Acrylonitrile + methanol*, *Acrylonitrile + 1,4-dioxane* and *Acrylonitrile + cyclohexane* mixtures respectively at 303K. From the measured data, related acoustical and thermodynamic excess parameters have been computed and the results of excess parameters are analyzed in the light of molecular interactions in the binary mixtures.

### MATERIALS AND METHODS

The liquid Acrylonitrile (solute) and methanol, 1,4-dioxane and cyclohexane (solvents) were of Analar grade samples and purified before use. The binary mixture of different mole fraction of the two components in the

Systems-I: Acrylonitrile+methanol, Systems-II: Acrylonitrile+1,4-dioxane and Systems-III: Acrylonitrile+cyclohexane respectively were prepared immediately before use. The velocity of ultrasonic wave (U) of frequency 10MHz and density ( $\rho$ ) in these mixtures were measured by employing Ultrasonic Time Intervalometer, UTI-10 ( Innovative instruments , Hyderabad ), and hydrostatic sinker method in the temperature range 10-40°C. Ultra thermostat U-10 maintained temperature of samples, constant to 0.1°C. A specially designed and fabricated double walled, metallic ultrasonic cell and glass cell along with 6- digit monopan balance permitted to achieve accuracy of 1 in 10<sup>-4</sup> m/s in velocity and 1 in 10<sup>-4</sup> gm in density measurement. An Ostwald's viscometer was used for the viscosity ( $\eta$ ) measurement of pure liquids and liquid mixtures with an accuracy of 0.0001Nm<sup>-2</sup>s. The viscometer was calibrated before used. All the precautions were taken to minimize the possible experimental error.

The various acoustical parameters such as Adiabatic compressibility ( $\beta_a$ ), Intermolecular free length ( $L_f$ ), Free volume ( $V_f$ ), Internal pressure ( $\pi_i$ ), Relaxation time ( $\tau$ ) and Gibb's energy ( $\Delta G$ ) has been calculated from the measured values of ultrasonic velocity (U), the density ( $\rho$ ) and viscosity ( $\eta$ ) of the medium using the following standard equations as:

$$\begin{aligned} \beta_a &= 1 / (U^2 \rho), & \text{----- (1)} & & L_f &= K_T (\beta_a)^{1/2} & \text{----- (2)} \\ V_f &= [M_{\text{eff}} U / K \eta]^{3/2} & \text{----- (3)} & & \pi_i &= bRT (K \eta / U)^{1/2} (\rho^{2/3} / M^{7/6}) & \text{----- (4)} \\ \Delta G &= (K_B T) \log (K_B T \tau / h) & \text{----- (5)} & & Z &= U \rho & \text{----- (6)} \\ \tau &= (4/3) \beta_a \eta & \text{----- (7)} & & & & \end{aligned}$$

Where  $K_T$  is a Jacobson's constant. Where  $M_{\text{eff}}$  is the effective molecular weight ( $M_{\text{eff}} = \sum m_i x_i$  in which  $m_i$  and  $x_i$  are the molecular weights and the mole fraction of the individual Constituents respectively).  $K$  is a temperature independent constant which is equal to  $4.28 \times 10^9$  for all liquids,  $b$  stands for cubic packing which is assumed to be 2 for all liquids, and  $T$  is the absolute temperature.  $K_B$  is the Boltzmann's constant and  $h$  has usual meaning.

#### Excess parameters ( $A^E$ ):

Represent the difference between the parameters of real mixtures ( $A_{\text{expt.}}$ ) and those corresponding to ideal mixtures ( $A_{\text{id.}}$ ).

$$A^E = A_{\text{expt.}} - A_{\text{id.}} \quad \text{..... (8)}$$

Where  $A_{\text{id}} = \sum A_i X_i$ ,  $i = 1, 2, 3, n$ .  $A_i$  is any acoustical parameters and  $X_i$  the mole fraction of the liquid components.

## RESULTS AND DISCUSSION

The values of ultrasonic velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) for the pure liquids used in this paper are compared with literature values and shown in the Table-1. Table-2 shows, the variation of excess compressibility ( $\beta_a^E$ ), excess free length ( $L_f^E$ ), excess internal pressure ( $\pi_i^E$ ), excess acoustic impedance ( $Z^E$ ), excess free volume ( $V_f^E$ ), excess relaxation time ( $\tau^E$ ) and excess Gibb's free energy ( $\Delta G^E$ ) for different mole concentration of solute (Acrylonitrile) for the system-I: (Acrylonitrile+methanol), system-II: (Acrylonitrile +1,4-Dioxane) and the system-III: (Acrylonitrile +Cyclohexane). The trend in excess or deviation parameters such as excess compressibility ( $\beta_a^E$ ), excess free length ( $L_f^E$ ), excess internal pressure ( $\pi_i^E$ ), excess acoustic impedance ( $Z^E$ ), excess free volume ( $V_f^E$ ), excess relaxation time ( $\tau^E$ ) and excess Gibb's free energy ( $\Delta G^E$ ) versus mole fraction of Acrylonitrile (solute) are shown in Fig.1-7. The excess thermodynamic properties of organic liquid mixtures depend on the chemical nature, size and shape of their constituent molecules.

In general,  $\beta_a^E$  values depend upon two factors; (i) Increase in free length due to loss of dipolar association, breaking up of hydrogen bonding and difference in size and shapes of component molecules, (ii) Decrease in free length due to dipole-dipole interaction, hydrogen bonding, association and complex formation between component molecules and also due to interstitial accommodation for unlike molecules if there is a difference in their size. An inspection of Table-2 reveals that, the first effect contributes to increase in interface between molecules in mixture. This would result the excess adiabatic compressibility ( $\beta_a^E$ ) is negative over the entire composition range of the mixture for all the systems investigated. The negative value of excess adiabatic compressibility indicate that the liquid mixture is less compressible than the pure liquids forming the solution and the molecules in this mixture are more tightly bound in the liquid mixture than in pure liquids. Thus negative value of excess adiabatic compressibility of this system indicates strong specific interaction between the component molecules and interstitial accommodation of small molecules in the voids created by bigger molecules.

Table – 1: Comparison of experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic Velocity (U) of pure liquids at 303K with literature values

Pure liquids	Density( $\rho$ )( Kg m <sup>-3</sup> )		Viscosity ( $\eta$ ) (10 <sup>-3</sup> NSm <sup>-2</sup> )		Velocity (U)(m/s)	
	Expt.	Literature	Expt.	Literature	Expt.	Literature
Acrylonitrile	806.60	-----	0.3060	-----	1425.00	-----
Methanol	776.10	777.70	0.5150	0.5030	1086.00	1087.60
Dioxane	1027.40	1028.10	0.8154	1.0100	1324.00	1323.00
Cyclohexane	772.30	763.70	0.6887	0.6895	1240.00	1243.30

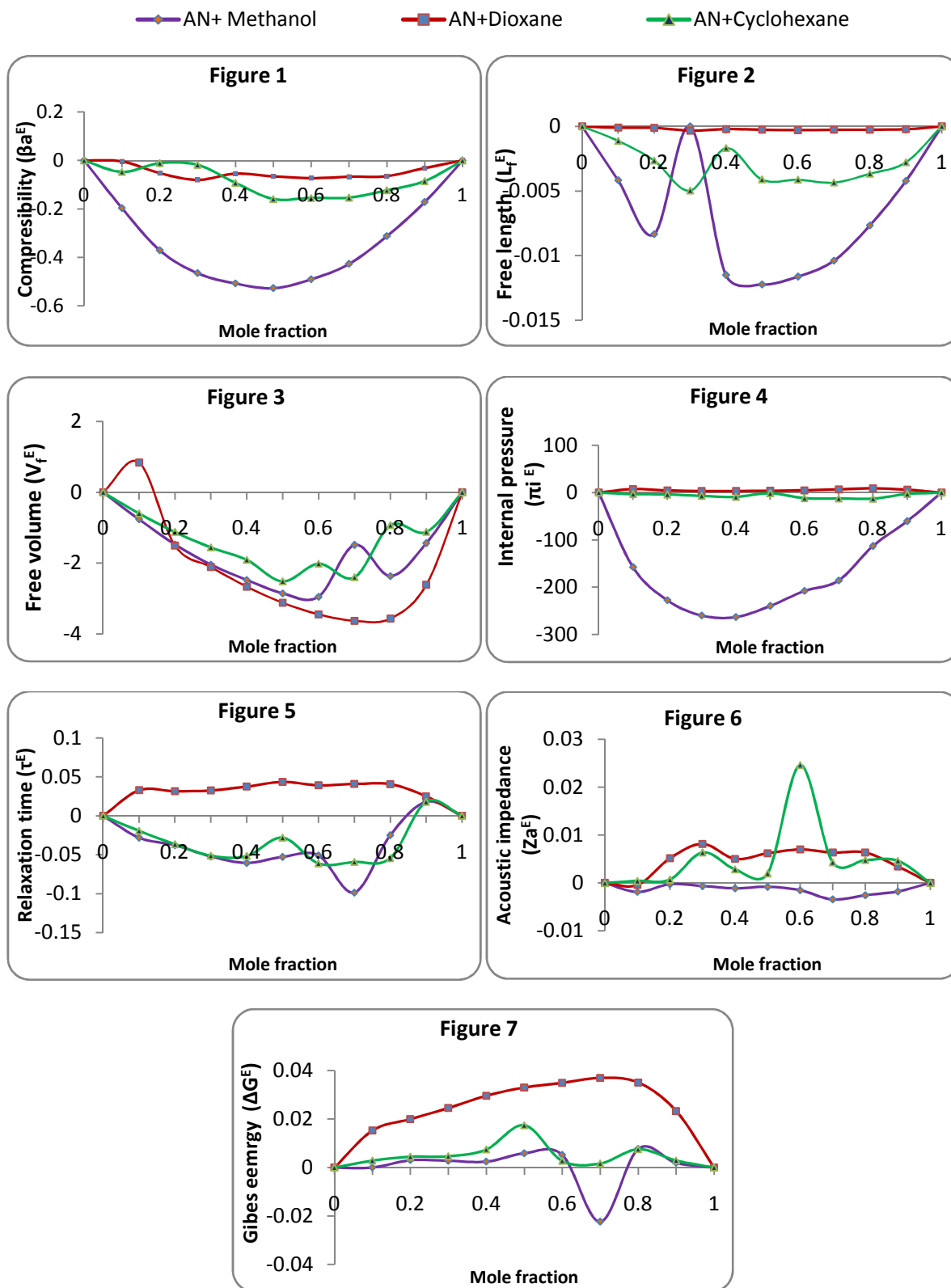
Table -2: The computed excess thermodynamic parameters at 303K for the systems I, II &amp; III respectively:

Mole fraction		$\beta a^E \times 10^{-10}$	$L_f^E \times 10^{-10}$	$V_f^E \times 10^{-7}$	$J_i^E \times 10^6$	$\tau \times 10^{-12}$	$Za^E \times 10^6$	$\Delta G^E \times 10^{-20}$
X <sub>1</sub>	X <sub>2</sub>	(m <sup>2</sup> N <sup>-1</sup> )	(m)	(m <sup>3</sup> .mole <sup>-1</sup> )	(Pa)	(S)	(Kgm <sup>-2</sup> s <sup>-2</sup> )	(K <sub>J</sub> mole <sup>-1</sup> )
<b>System-I: Acrylonitrile + Methanol</b>								
0	1	0	0	0	0	0	0	0
0.1	0.9	-0.1964	-0.0041	-0.7617	-157.65	-0.0282	-0.0018	0.0001
0.2	0.8	-0.3708	-0.0083	-1.4720	-227.45	-0.0378	-0.0002	0.0030
0.3	0.7	-0.4652	-0.01050	-2.0436	-259.83	-0.0523	-0.0006	0.0028
0.4	0.6	-0.5076	-0.0115	-2.4745	-263.08	-0.0606	-0.0011	0.0024
0.5	0.5	-0.5270	-0.0122	-2.8542	-239.63	-0.0529	-0.0008	0.0059
0.6	0.4	-0.4904	-0.0116	-2.9468	-207.93	-0.0510	-0.0015	0.0052
0.7	0.3	-0.4268	-0.0103	-1.4840	-185.91	-0.0986	-0.0034	0.0223
0.8	0.2	-0.3122	-0.0076	-2.3653	-112.88	-0.0250	-0.0025	0.0077
0.9	0.1	-0.1716	-0.0042	-1.4326	-60.39	-0.0179	-0.0017	0.0019
1	0	0	0	0	0	0	0	0
<b>System-II: Acrylonitrile + 1,4-Dioxane</b>								
0	1	0	0	0	0	0	0	0
0.1	0.9	-0.0040	-0.0001	-0.8423	7.2848	0.0327	0.0004	0.0152
0.2	0.8	-0.0527	-0.0001	-1.4991	4.5472	0.0315	0.0051	0.0199
0.3	0.7	-0.0806	-0.0003	-2.1072	3.1798	0.0325	0.0081	0.0245
0.4	0.6	-0.0547	-0.0002	-2.6613	3.2944	0.0374	0.0050	0.0296
0.5	0.5	-0.0659	-0.0002	-3.1142	3.6630	0.0434	0.0062	0.0330
0.6	0.4	-0.0733	-0.0002	-3.4424	4.6416	0.0391	0.0069	0.0348
0.7	0.3	-0.0675	-0.0002	-3.6251	6.6432	0.0407	0.0063	0.0369
0.8	0.2	-0.0649	-0.0002	-3.5617	8.8328	0.0405	0.0063	0.0350
0.9	0.1	-0.0316	-0.0002	-2.6044	5.8614	0.0249	0.0034	0.0233
1	0	0	0	0	0	0	0	0
<b>System-III: Acrylonitrile + Cyclohexane</b>								
0	1	0	0	0	0	0	0	0
0.1	0.9	-0.0470	-0.0011	-0.5968	-3.1497	-0.0193	0.0004	0.0028
0.2	0.8	-0.0106	-0.0026	-1.1193	-3.9441	-0.0364	0.0007	0.0044
0.3	0.7	-0.0177	-0.0049	-1.5562	-7.0021	-0.0512	0.0063	0.0046
0.4	0.6	-0.0923	-0.0016	-1.9066	-8.9948	-0.0516	0.0028	0.0074
0.5	0.5	-0.1587	-0.0041	-2.5127	-1.2585	-0.0281	0.0020	0.0174
0.6	0.4	-0.1544	-0.0041	-2.0170	-11.7182	-0.0611	0.0246	0.0027
0.7	0.3	-0.1532	-0.0043	-2.3987	-12.4459	-0.0592	0.0043	0.0016
0.8	0.2	-0.1230	-0.0036	-0.9306	-12.8766	-0.0543	0.0047	0.0075
0.9	0.1	-0.0849	-0.0027	-1.1161	-2.9833	-0.0181	0.0046	0.0029
1	0	0	0	0	0	0	0	0

The overall excess free volume ( $V_f^E$ ) is also negative for all the systems over the entire composition range of the mixture. The overall negative value of excess free volume ( $V_f^E$ ) for the systems, suggests the component molecules are more closed together in the liquid mixture than in the pure liquids forming the mixture, indicating that, strong attractive interactions between component molecules such as hydrogen bonding and dipole-dipole interactions. The variation of excess free length ( $L_f^E$ ) is negative over the entire range of composition, for all the systems. The negative value of excess free length ( $L_f^E$ ) for all the systems indicates structural readjustment in the liquid mixture toward a less compressible phase of fluid and closer packing of the molecule. This aspect further supports the variation of other excess parameters such as, excess internal pressure ( $\pi_i^E$ ), excess acoustic impedance ( $Za^E$ ), excess relaxation time ( $\tau^E$ ) and excess Gibbs free energy ( $\Delta G^E$ ).

The trend of figure-1 and 2 shows that  $\beta a^E$  and  $L_f^E$  are increasingly negative as Acrylonitrile (AN) mole fraction is increased. Thus, strong dipolar interactions are restricted more and more. However  $V_f^E$  for all the systems are mostly negative, existing weak dispersive interactions. Such existence of weak interactions was confirmed by Karthikeyan et al [16].

Fig.1-7: Graphs for excess parameters of adiabatic compressibility, free length, free volume, internal pressure, relaxation time, acoustic impedance and Gibb's energy for System-I, System-II and System-III respectively are as shown below:



### CONCLUSION

The dependence of ultrasonic velocity and other derived parameters on composition of the mixtures is indication of the presence of molecular interactions. Weak dispersive type interactions are confirmed in the systems investigated. Components maintain their individuality in the mixtures of all the systems investigated. All the experimental

determinations of acoustic parameters and their excess values are strongly correlated with each other. In this paper, the excess thermodynamic parameter such as excess compressibility ( $\beta_a^E$ ), excess free length ( $L_f^E$ ), excess internal pressure ( $\pi_i^E$ ), excess acoustic impedance ( $Z^E$ ), excess free Volume ( $V_f^E$ ), excess relaxation time ( $\tau^E$ ) and excess Gibb's free energy ( $\Delta G^E$ ) for different mole concentration of solute (Acrylonitrile) for the above binary mixtures are evaluated and these parameters suggests the presence of weak molecular interactions. This molecular interaction is primarily of dipole –induced dipole type. Further in all the systems, the non-polar cyclohexane and 1, 4-dioxane behaves as structure breaker for associated Acrylonitrile.

#### Acknowledgement

Author VDB [File No.: F-47-919/09(WRO)] acknowledge the financial assistance from UGC, in the form of Minor Research Project grant.

#### REFERENCES

- [1]G Padmanabhan, R Kumar, V Kannappam& S Jaykumar (2012). *Ind Jour of Pure and appli Phy*, 50, 899-906.
- [2]Ali A, Hyder S & Nain A K, (2002). *Indian J Phys*, 76B (5), 661-667.
- [3]Bhandakkar V D, Tabhane V A & Sharda Ghosh (2003). *Ind Jour Pure and Appli Phys*, 41, 849 -854.
- [4]Ali A and Mohd Tariq (2006). *Pure and applied Ultrasonic*. 28, 99-104.
- [5]Selvakumar M & Krishna Bhat D (2008). *Ind Jour of Pure and appli Phy*. 46, 712-718.
- [6]John George, Sastry N V, Patel S R & Valand M K (2002). *J Chem Eng*. 47, 262-269.
- [7] Ali A, Hyder S & Akhtar Y (2005). *Indian J Phys*, 79(2), 153-156.
- [8]Vogel A I, *A Text book of Practical Organic chemistry 5th Edn (John Willey, New York) 1989*.
- [9] Bhandakkar V D and Rode Sweta (2012). *Advs in Appli Sci Res Jour, Pelagia Research Library*. 3(5), 3223-3229.
- [10] Bhandakkar V D (2012). *International Jour of Scientific res, Jour of Appli Phys*. 1(5), 38-43.
- [11] G R Bedare, V D Bhandakkar& B M Suryavanshi (2013). *Der Pharmacia Sinica*, 4(1),97-101.
- [12] G R Bedare, V D Bhandakkar& B M Suryavanshi (2013). *Pelagia Research Library, Der Chemica Sinica*, 4(1), 132-137.
- [13] G R Bedare, V D Bhandakkar & B M Suryavanshi (2012). *International Journal of Material Science Engineering*. 42(, 012028, IOP Publishing, doi: 10.1088/1757-899X/42/1/012028.
- [14] N R Pawar, O P Chimankar & V D Bhandakkar (2012). *International Journal of Material Science Engineering*, IOP Publishing, doi:10.1088/1757- 899X/42/1/01203, 42, 012030.
- [15] N R Pawar, Chimankar O P & Bhandakkar V D (2012). *Ind Jour Pure Appli Ultrasonics*. 34, 2(3), 49-52.
- [16] Karthikeyan V & Palaniappan L (2005). *J Phys.*, 79(2), 153-156.